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Recent advances in reuse of waste material as substrate to produce biohydrogen by purple non-sulfur (PNS) bacteria

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ABSTRACT

Hydrogen is the fuel of the future mainly due to its high conversion efficiency, recyclability and non-polluting nature. Biological hydrogen production processes, mostly mediated photosynthetic bacteria, are more favorable candidates for biological hydrogen production due to their high conversion efficiency and versatility in the substrates (including wastewater) they can utilize. The potential utilization of waste material is being investigated extensively with suitable bioprocess technologies for providing cheaper raw materials with simultaneous waste treatment and bioremediation. Thus, this review article summarizes the biohydrogen production metabolism of purple non-sulfur (PNS) bacteria and research works involving biohydrogen production using various wastes such as tofu wastewater, palm oil mill effluent, olive mill wastewater, brewery wastewater, etc. by photosynthetic PNS bacteria. Waste materials used, yields and rates are reviewed, together with a discussion of the economics and perspectives of biohydrogen production from waste materials.

Contents

1. Introduction

Today, global energy requirements are mostly dependent on fossil fuels (about 80% of the present world energy demand). This will eventually lead to the depletion of worldwide fossil energy reserves. In addition, combustion of fossil fuels has caused global climate change and health problems due to the emission of significant amounts of volatile organic compound (VOC), CO_2, CO, and NO_x [1]. In order to remedy the depletion of fossil fuels and their negative impact on the environment, hydrogen is considered as a viable alternative fuel and energy carrier of the future. Unlike other fossil-based chemical and gaseous fuels, hydrogen produces only water when it combusted as fuel or converted to electricity [2]. Besides, hydrogen has a high energy yield of 122 kJ/g, which is 2.75 times greater than that of hydrocarbon fuels [3]. Moreover, its low heating value (LHV) is 4, 2.8 and 2.4 times higher than coal, gasoline and methane, respectively [4].

At present, 40% of hydrogen is produced from natural gas, 30% from heavy oils and naphtha, 18% from coal, 4% from electrolysis and around 1% from biomass [5]. Each method of hydrogen production requires a source of energy such as thermal, electrolytic or photolytic. However, methods that use thermal and electrolytic source are energy-intensive as they require high operating temperature [6]. Biological hydrogen production offers unique advantages as compared to chemical processes as it is clean, efficient and renewable, which can be considered as the most environmental friendly route to produce biohydrogen [7]. Through appropriate

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biological process, a number of organic wastes such as dairy wastewater and olive mill wastewater could be reused [8,9]. Thus, biohydrogen produced from the renewable resources could minimize waste accumulation and maintain a sustainable ecosystem, to meet the increasing needs for harnessing renewable energy [10].

Biological hydrogen production is classified into 4 categories, namely biophotolysis, dark fermentation, photofermentation and hybrid systems combining dark and photofermentation. A biophotolysis process is a biological process which utilizes solar energy and algae to split water molecule into hydrogen ion and oxygen ion [11]. The oxygen produced in biophotolysis process inactivates the H_2-producing systems in algae, leading to lower yield of biological hydrogen [6]. Dark fermentation uses fermentative bacteria to breakdown carbohydrate-rich substrates to hydrogen and other products such as acids and alcohols but gives lower yield of biohydrogen [12]. Biohydrogen production through photofermentation process is mainly due to the presence of nitrogenase under nitrogen-deficient condition using light energy and organic compound as substrate [13]. Lastly, a new hybrid biohydrogen production process has very recently been studied extensively, which is carried out based on the concept and practice of a microbial fuel cell (MFC) [14–21].

Among these technologies, photofermentation is a favorable process for large scale production as it allows high substrate conversion efficiencies and its capability to use wide variety of substrates (including wastewater) either for growth or biohydrogen production [22]. Moreover, photosynthetic bacteria is suitable to be used for converting light energy into H_2 using organic waste as a substrate in batch processes, continues or immobilized whole cell system [13]. However, wastewater pre-treatment may be required prior to photofermentation biohydrogen production due to either the toxic nature of the effluent, or its opaqueness [23].

Biohydrogen production is a novel and promising approach to substitute depleting fossil fuels to meet increasing energy demands in the future by virtue of the fact that it provides a clean energy source and is able to utilize natural resources and waste materials. On the basis of these facts, this review summarizes the various types of carbohydrate-rich waste and raw materials that could be utilized for biohydrogen production by PNS bacteria, together with a discussion of the economics and perspectives of biohydrogen production from waste materials.

2. PNS bacteria

Some photo-heterotrophic bacteria are capable of converting organic acids (acetic, lactic and butyric) to biohydrogen (H_2) and carbon dioxide (CO_2) under anaerobic conditions in the presence of light. Therefore, the organic acids produced during the acidogenic phase of anaerobic digestion of organic wastes can be converted to H_2 and CO_2 by those photosynthetic anaerobic bacteria.

PNS bacteria constitute a non-taxonomic group of versatile organisms which can grow as photoheterotrophs – switching from one mode to another depending on available conditions such as degree of anaerobiosis, carbon source (CO_2 for autotrophic growth, organic compounds for heterotrophic growth), and light source (needed for phototrophic growth). PNS bacteria requires lesser energy (+8.5 kJ/mol hydrogen for lactate) for generating biohydrogen compared to water splitting by algae [23].

There are various PNS bacteria that participate in biological hydrogen generation by photofermentation such as *Rhodobacter sphaeroides* O.U.001, *Rhodobacter sphaeroides* RV, *Rhodobacter capsulatus*, *Rhodobacter sulfidophilus*, *Rhodopseudomonas palustris*, *Rhodospirillum rubrum* etc. Among these PNS bacteria, *R. sphaeroides* remains the most promising bacteria in biohydrogen production under light condition. It is a typical anoxygenic phototrophic bacterium which is widely used for photo-biohydrogen production from organic wastewater, including olive oil wastewater and the effluent of anaerobic treatment [24–26].

H_2 production by *R. sphaeroides* and other PNS bacteria occurs under light condition in the presence of an inert, anaerobic atmosphere (such as argon), from the breaking-down of organic substrates (malate, acetate, butyrate, propionate and lactate) or industrial effluents. The culture medium should be under nitrogen limitation (inducing high C/N ratio), which forces the bacteria to 'dump' the excess energy and reducing power through production of hydrogen.

Two criteria are used for evaluating the biohydrogen production performance of a specific substrate. The first is the hydrogen gas production rate, and the second criteria is the substrate conversion efficiency. On the basis of available literature, the highest conversion efficiency was obtained using malic acid as a carbon source using *R. sphaeroides* O.U.001 [6].

R. capsulatus, a PNS bacteria was improved for hydrogen production by eliminating polyhydroxyalkanote (PHA) synthesis and knocking out the uptake hydrogenase [27]. Another improvement strategy used in PNS bacteria involved the genetic modification of the electron transfer chains in *R. capsulatus*. This study has proven that the modification increases nitrogenase expression and hydrogen production by 2-fold [28].

3. Nitrogenase and hydrogenase enzyme system

Biohydrogen production by photosynthetic bacteria is mainly mediated through nitrogenase enzyme complex, evolved to catalyze N_2 fixation:

$$2H^+ + 2e^- + 4ATP \rightarrow H_2 + 4ADP + 4P_i \quad (1)$$

The activity of the enzyme is inhibited in the presence of oxygen, ammonia, or at high N/C ratio [29]. It catalyzes biohydrogen production only in the absence of molecular nitrogen as shown in Eq. (1), while oxygen irreversibly destroys it. The presence of ammonium inhibits nitrogenase activity by suppressing the synthesis of nitrogenase [30]. Therefore, the process requires ammonium limited and anaerobic conditions. The metabolism shifts to utilization of organic substances for cell synthesis rather than hydrogen production in the presence of high nitrogen concentrations resulting in excess biomass growth and reduction of light diffusion. Ammonium salt concentrations as low as 20 μM have been found to rapidly inhibit existing nitrogenase activity in *R. sphaeroides*. However, the inhibition is reversible and nitrogenase activity could be recovered once ammonium is consumed or removed [22].

It was reported that the presence of carbonate enhanced ammonia removal and stimulated hydrogen production [31]. Two-stage ammonia removal and hydrogen production processes have been suggested for hydrogen production from high ammonia wastewater [32]. Nitrogenase of most PNS bacteria, especially *R. sphaeroides* contain molybdenum centers and thus the availability of molybdenum is usually crucial for this enzyme. However, if the bacteria is capable of synthesizing 'alternative' nitrogenases, molybdenum deficiency may be tolerated, as reported by Yakunin et al. [33] for *R. capsulatus*.

Hydrogenase on the other hand catalyzes the following simplest redox reaction in either direction:

$$H_2 \Leftrightarrow 2H^+ + 2e^- \quad (2)$$

In the presence of suitable electro acceptors, the reaction are capable to consume H_2; under strict anaerobiosis, the reaction are prone to produce H_2. The hydrogenases are distributed into two classes of distinct phylogenetic origin, the [NiFe]-hydrogenases and the [FeFe]-hydrogenases [34]. Hydrogenase enzyme in PNS bacteria

Table 1
Hydrogen yield on waste materials by different PNS bacteria.

Strain	Waste material used	Light intensity (klux)	Waste Concentration (%v/v)	Maximum yield of H_2 production (L/L WW)	Process	Reference
Rhodobacter sphaeroides						
R. sphaeroides O.U. 001	Dairy wastewater	9	40	3.2	Batch	[8]
R. sphaeroides O.U. 001	Brewery wastewater	9.0	10	0.22	Batch	[38]
R. sphaeroides O.U. 001	Olive mill wastewater	15.4	2	13.9	Batch	[39]
R. sphaeroides O.U. 001	Sugar refinery effluent	15.4	20	0.13	Batch	[40]
R. sphaeroides O.U. 001	Distillery wastewater	4.0	10	0.1	Semi–continuous	[44]
R. sphaeroides O.U. 001	Olive mill wastewater	–	4	8	Batch	[45]
R. sphaeroides RV	Tofu wastewater	8.5	50	4.32	Batch	[36]
R. sphaeroides RV	Acid hydrolyzed wheat starch	3.0	–	1.78	Batch	[41]
R. sphaeroides RV	Tofu wastewater	8.0	–	1.9	Batch	[46]
R. sphaeroides RV	Enriched lactate liquor	10	–	100[b]	Batch	[47]
R. sphaeroides RV	Lactate from MSW[a]	10	–	1.2[b]	Batch	[47]
R. sphaeroides RV	Fruit & vegetable wastes	–	–	100[b]	Batch	[48]
R. sphaeroides AR-3	Tofu wastewater	6.0–7.0	–	1.73	Batch	[37]
R. sphaeroides NRLL	Acid hydrolyzed wheat starch	3.0	–	1.15	Batch	[41]
R. sphaeroides DSZM	Acid hydrolyzed wheat starch	3.0	–	1.35	Batch	[41]
Rhodopseudomonas sp.						
Rhodopseudomonas sp.	Sugarcane wastewater	3.0	–	45[c]	Batch	[49]
Rhodopseudomonas sp.	Potato starch	3.0	–	30[c]	Batch	[49]
Rhodopseudomonas sp.	Whey	3.0	–	25[c]	Batch	[49]
Rhodopseudomonas palustris PBUM001	Palm oil mill effluent	4.0	100	0.66	Batch	[43]

[a] Municipal solid waste.
[b] Expressed in evolution rate, mL H_2 g^{-1} dry weight h^{-1}.
[c] Expressed in mL H_2 mg^{-1} dry weight h^{-1}.

is an uptake hydrogenase which utilizes hydrogen gas and therefore is antagonistic to nitrogenase activity [22]. Uptake hydrogenase activity should be limited for enhanced hydrogen gas production. Although hydrogenases are present in PNS bacteria, biohydrogen production through photofermentation by these bacteria is mainly mediated by nitrogenase [6].

4. Waste utilization by PNS bacteria for biohydrogen production

The main aim of biohydrogen production studies using *R. sphaeroides* and other PNS bacteria is to develop commercially viable hydrogen production processes. Studies were conducted by researchers to identify the suitability of different processes and to optimize different process parameters. Among the physicochemical parameters affecting biohydrogen production by PNS bacteria as reported by various researchers are: carbon-to-nitrogen ratio, inoculum age, light intensity, temperature, batch or continuous operation model, and suspended or immobilized cells [6].

Recently, the economic production of hydrogen from wastewaters show great potential because producing a product from waste could reduce waste treatment and disposal costs [35]. Different photosynthetic and fermentative bacteria can utilize waste materials like municipal solid wastes, industrial effluents and sewage sludge. However, one major problem encountered in biohydrogen production from industrial effluents is the dark color of the wastewater, which could reduce light penetration. High ammonia concentration is another concern which inhibits the nitrogenase enzyme, thus reducing the hydrogen productivity. High organic matter content (COD) and the presence of some toxic compounds (heavy metals, phenolics and PAH) in food and manufacturing industrial wastewater may require pre-treatment before biohydrogen production. Little is known on the metabolism of complex wastes but studies of biohydrogen production from wastewater are numerous and a few examples of the recent studies involving PNS bacteria such as *Rhodobacter* and *Rhodopseudomonas* species are summarized in Table 1 [8,6,36–49].

Zhu et al. [36] utilized a tofu wastewater (TWW), which is a carbohydrate and protein rich effluent, as a substrate in biohydrogen production by a wild type anoxygenic phototrophic bacterium (*R. sphaeroides* RV). Biohydrogen was produced at a high yield of 1.9 L/L WW with 40% of total organic carbon (TOC) removal (from 8810 mg/l to 5288 mg/l) within 84 h. After the tofu wastewater was diluted by 50%, the TOC removal ratio and hydrogen yield were increased to 66% and 4.32 L/L WW, respectively. This study proved that some inhibitory factors to hydrogen production by *R. sphaeroides* RV existed. Therefore, the inhibitory factors were also diluted through the dilution of the tofu wastewater, resulted in increasing hydrogen production activity and TOC removal ratio [36].

Biohydrogen generation from tofu wastewater (TWW) was also studied by Zheng et al. [37] using wild type strain of *R. sphaeroides* and glutamine autotrophic mutant- *R. sphaeroides* AR-3. Wild- type *R. sphaeroides* was observed to give average production rate of 6.7 mL/L h and total hydrogen production of 0.81 L/L WW within 120 h. However, mutant AR-3 gave higher biohydrogen rate and yield up to 14.2 ml/L h and 1.73 L/L WW, respectively. This study demonstrated that wild- type *R. sphaeroides* was not suitable for biohydrogen production from TWW that normally contains 3–4 mmol/L of NH_4^+ because the presence of NH_4^+ at a concentration of 2 mmol/L or above would inhibit biohydrogen production due to its suppression on the syntheses of nitrogenase [37].

Seifert et al. [38] studied the reuse of brewery wastewater (BWW) as substrate in biohydrogen production by R. *sphaeroides* O.U.001. Best substrate yield were obtained (0.22 L/L WW), after BWW was filtered to a concentration around 10% (v/v). At higher concentration (20% (v/v)), the colour of the medium became darker and reduced the access of light which decreased the photogenerated hydrogen. In addition, activity of nitrogenase reduced significantly with increasing NH_4^+ (above 1 mM NH_4^+) in reaction medium and consequently lowered the biohydrogen production. It

Table 2
Cost comparison of biohydrogen production processes with that of conventional processes.

Type of energy	Raw materials used/resources	Conversion efficiency (%)	Unit cost of energy content of fuel (US $/MBtu)	References
Photobiological hydrogen	H_2O & organic acids	10	10	[58]
Fermentative hydrogen	Molasses	28.34	30	[59]
Fermentative ethanol	Molasses	15–30	31.5	[59]
Fast pyrolysis for H_2 production	Coal & biomass	–	4	[60]
H_2 from advanced electrolysis	H_2O	–	10	[60]
H_2 from cyclical thermal decomposition of steam	H_2O	–	13	[60]
H_2 from photochemical cells	Organic acids	–	21	[60]
Gasoline	Crude petroleum	–	6	[60]

was also reported that the amount of biomass was doubled whereas no hydrogen was observed at a very high concentrations of NH_4^+, directly indicated that ammonium ions could only be involved in biomass generation [38].

Seifert et al. [8] conducted an experiment that produced biohydrogen from dairy wastewater (DWW) with the presence of R. *sphaeroides* O.U.001. It was reported that increase of dairy waste concentration up to 40% was able to double (filtered water) or triple (non-filtered water) the amount of biohydrogen produced. Study showed that the highest volume biohydrogen (3.2 L/L WW) was obtained at concentration of 40% (v/v) after pretreatment. Total inhibition of the process was observed at the dairy waste concentration of 60% (v/v), contained 1.7 mM nitrogen in the NH_4^+. Such high concentration of nitrogen can inhibit significantly the biohydrogen production process [8].

Photobiological hydrogen production from olive mill wastewater (OMWW) using R. *sphaeroides* O.U.001 was investigated by Eroglu et al. [39]. This study was conducted by diluting OMWW in the range of 1% to 20%. OMWW could be utilized as a sole substrate source as it has high carbon-to-nitrogen ratio and high organic contents such as sugars and organic acids [6]. 2% OMWW resulted in the highest biohydrogen production potential of 13.9 L/L WW with 35% COD removal ratio achieved. Biohydrogen could not be produced in concentrated media (containing more than 4% OMWW) due to the presence of high amounts of inhibitory substances and their relatively dark color which reduced light penetration [6].

Photoproduction of biohydrogen from pre-treated sugar refinery wastewater (SRWW) was studied by Yetis et al. [40] in a column photo-bioreactor using *R. sphaeroides* O.U.001. The biohydrogen production rate was 3.8 mL/L h at 32 °C in batch operation with 20% diluted SRWW. The results of purity analysis showed that the biogas contained 99% hydrogen gas and 1% carbon dioxide in argon-free basis [40]. Addition of malic acid into SRWW enhanced the production rate to 5 mL/L h. In another study, Kapdan et al. [41] used three different pure strains of *R. sphaeroides* (RV, NRLL and DSZM) in sugar solution derived from acid hydrolysis of ground wheat starch for producing biohydrogen. *R. sphaeroides* RV resulted in the highest hydrogen yield with 1.23 mol H_2/mol glucose among the other pure cultures. Effect of sugar concentration on biohydrogen formation by *R. sphaeroides* RV was also studied by varying sugar concentration between 2.2 g/L and 22 g/L. Biohydrogen production was enhanced together with increase of sugar concentration until 8.5 g/L but higher sugar content would eventually inhibit biohydrogen production due to the high volatile fatty acid concentration formed at higher sugar contents [41].

The potential of using palm oil mill effluent (POME) as the main substrate to produce biohydrogen has been revealed as it contains hemicelluloses and lignocelluloses material [42]. Therefore, research has been carried out for producing biohydrogen by *Rhodopseudomonas palustris* PBUM001 from POME by Jamil et al. [43]. It was reported that optimal biohydrogen production and COD reduction were achieved with POME concentration at 100% (v/v) as it has higher content of organic acids compared to the diluted POME. The cumulative biohydrogen production and COD removal were 0.66 L/L WW and 30.54%, respectively under optimum conditions of 100% (v/v) POME concentration, 4.0 klux light intensity, initial pH of 6, 10% (v/v) inoculum size and 250 rpm agitation speed. This research also showed that light intensity did not affect cumulative biohydrogen production at lower concentration of POME [43].

5. Discussion and outlook

Current world hydrogen production is approximately 500 Bm^3 (billion cubic meters) or 44.5 million tons per annum, representing 2% of primary energy demand [50]. It is estimated that the use of hydrogen in fuel cell vehicles (FCVs) and light trucks could substitute the consumption of 18.3 million barrels of petroleum per day by year 2040 [51]. The advantage of using FCVs is that they reduce emissions as compared to current vehicle with carbon emissions drop to near zero and less emissions of NO_x. In major cities, reductions in local air pollution could improve the quality life for citizens significantly and reduces health care cost. However, FCVs are not economically compatible with conventional vehicles currently as they are about three times more expensive than conventional vehicles in engine cost [52].

The US Department of Energy (DOE) Hydrogen Program has set a cost goal for hydrogen in the range of $14/GJ-$21/GJ, including production, delivery and dispensing. This is the level at which US DOE estimates that hydrogen will be cost competitive with petroleum fuels [53]. Under the US DOE funding, preliminary assessments of a conceptualized two stage indirect biophotolysis system and an indirect single stage process utilizing microalgal cultures was reported to the International Energy Agency (IEA) [54,55]. Based on prior studies for algal mass cultures for fuels production plus a separate hypothetical and actual photochemical process analysis, the average production cost stood at $10 and $15/GJ H_2 respectively for the two-stage and single stage process.

By comparison, the cost of gaseous hydrogen using photovoltaic-electrolysis for the desert south west, projected to the year 2010, were estimated at $19/GJ, or almost 2 times higher than estimated here for an algal system [56]. Economic analysis on a biohydrogen production plant from lignocellulosic feedstock showed an estimated overall biohydrogen production cost of $26.3/GJ for production of 312 tonne H_2/year. The estimation was done on the basis of biomass acquisition at zero value, zero hydrolysis costs and excludes personnel and civil works costs, which all account for a certain cost factors [57].

Benemann [58], Tanisho [59] and Bockris [60] also calculated the energy cost by different biological as well as other hydrogen generation processes as compared to conventional fuels as summarized in Table 2 [58–60]. Biohydrogen from coal and natural gas appeared to be the most economical sources when compared with other sources. Nevertheless, the fact that various photosynthetic bacteria, especially the extensively studied *Rhodobacter sp.* highlighted earlier in the text, have the ability to utilize low or zero cost

waste materials like municipal solid wastes, industrial effluents or, sewage sludge has helped photobiological hydrogen production to stand out from the rest of the processes. Utilization of waste as carbon source has significant advantages as it reduces the photobiological hydrogen production cost and wastewater treatment cost. Besides, it also represents an attractive alternative solution to the increasing consciousness in environment preservation and global efforts towards industrial waste minimization and a more effective municipal waste treatment.

Despite reports of impressive hydrogen production yields, with essentially stoichiometric conversion of substrates to hydrogen, little data is available on true photosynthetic efficiencies under ideal and high-light conditions. Besides, low solar energy conversion efficiencies and the inherent high energy demand of nitrogenase system are the few uncertainties in photobiological hydrogen production. Another obstacle would be that complexity of the composition of the wastewater, which leads to difficulty in understanding how the substrates in the wastewater were integrated in the process of biohydrogen production. The detailed analysis was also difficult for the biohydrogen production due to the presence of various carbohydrates, protein, volatile acids and other organic compounds [46]. In addition, high ammonia concentration could inhibit the nitrogenase enzyme and colour of wastewater could reduce the light penetration, which reduces the biohydrogen productivity. Also, the limits imposed by the economic and social frameworks present obvious limitations to sustainable practices that could be applied in the industries [61,62], especially in most of the developing countries. Consequently, there is usually no economic incentive to develop waste free bioprocesses [62].

To overcome the above obstacles and improve biohydrogen yield, a number of scientific advances and technical breakthroughs are required. Hybrid fermentation technology which combined dark fermentation and photofermentation process might be one of the most promising routes for the enhancement of biohydrogen production. In hybrid fermentation, the anaerobic fermentation of carbohydrates produces intermediates (low molecular weight organic acids) which can be converted into biohydrogen by the photosynthetic bacteria [12]. Eroglu et al. [45] conducted their experiment in a hybrid fermentation technology using olive mill wastewater, with a three fold increase in biohydrogen production when compared to photofermentation alone.

It is important to note that the production of biohydrogen using waste materials could only be realized if it is subsidized, externalities are factored in, biohydrogen produced is successfully designed for commercial reuse and, most importantly, the government takes the initiative in legislating for a sustainable industrial development.

6. Conclusion

The major obstacles in biohydrogen production from wastes are low rates and yields of biohydrogen formation. Thus, tremendous progress were carried out in order to increase biohydrogen production by selecting more effective microorganisms, developing more efficient processing schemes, improving the light utilization efficiency, etc. The future of hydrogen economy is dependent on the availability of a low cost and environmentally friendly source of hydrogen [63]. In addition, fossil fuel costs, environmental concerns, social acceptance, and the growth of hydrogen economy can indirectly contribute to the economic viability of photofermentation biohydrogen production [64]. Of course, a long-term major development effort is required to eventually bring about an economically feasible photobiological hydrogen production, through sustainable photo-fermentation by the favorable PNS bacteria utilizing various low- or zero cost sources of wastewater and waste materials.

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